

## TITLE OF THE INVENTION

SEMICONDUCTOR DEVICE AND MANUFACTURING METHOD THEREOF

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application is based upon and claims the  
5 benefit of priority from the prior Japanese Patent  
Application No. 2001-230311, filed July 30, 2001,  
the entire contents of which are incorporated herein  
by reference.

### BACKGROUND OF THE INVENTION

#### 10 1. Field of the Invention

The present invention relates to a semiconductor  
device and manufacturing method thereof, and more  
particularly, to a semiconductor device employing a  
fluorine-doped silicon oxide layer as an interconnec-  
15 tion insulating layer, and a method of manufacturing  
the same.

#### 2. Description of the Related Art

In prior art semiconductor devices,  $\text{SiO}_2$  layer  
has been used as an insulating layer to electrically  
20 isolate interconnections. Such an  $\text{SiO}_2$  layer is  
primarily produced from source gas, for example, silane  
( $\text{SiH}_4$ ) and tetraethoxysilane (TEOS) by a low pressure  
or atmospheric pressure chemical vapor deposition  
(CVD) technique. Particularly, plasma chemical vapor  
25 deposition can produce an  $\text{SiO}_2$  layer at a low  
temperature of about  $400^\circ\text{C}$ , using TEOS and  $\text{O}_2$ , and the  
 $\text{SiO}_2$  layer produced in this way has been widely used.

Further, as compared with other thin layer producing methods, the CVD method often uses high purity gas as a reaction source, and provides high quality layers.

However, as microstructure of semiconductor elements has become widespread in recent years, concern about reduction of signal transmission speed has arisen. This implies a problem that reduced interconnection space increases the capacitance between interconnections and reduces signal transmission speed. The reduction in signal transmission speed seems to be one of the negative factors in increasing the performance of semiconductor devices. Therefore, to solve the problem, it is essential to reduce permittivity of the insulating layer formed between interconnections to the lowest possible value.

To reduce the permittivity, in recent years, fluorine-doped silicon oxide or fluorine-doped silicate glass (FSG) has been developed together with the parallel plate CVD technique or high density plasma CVD technique (HDP-CVD). As a method of producing high-density plasma, use of electron cyclotron resonance (ECR) or the inductive coupled plasma (ICP) coil or helicon wave, for example, has been reported.

FIG. 1 shows a sectional view of Cu multi-layer interconnection using a conventional FSG layer. In the same drawing, reference number 81 indicates an FSG layer and likewise, 82 indicates a barrier metal layer,

83 indicates a Cu interconnection in a lower layer, 84 indicates a silicon nitride layer, 85 indicates an FSG layer, 86 indicates another barrier metal layer, 87 indicates a Cu interconnection of an upper layer, 88 indicates another silicon nitride layer and 89 indicates a silicon substrate, respectively. The Cu interconnections 83 and 87 are dual damascene interconnections.

In the FSG layer, as has been reported, the higher the fluorine (F) density, the lower the permittivity, and at the same time, moisture absorption increases. As the moisture absorption of FSG layers 81 and 85 increases, moisture ( $H_2O$ ) is taken into these FSG layers. And, H caused by the moisture reacts with F contained in these FSG layers, and HF is liberated from the FSG layers 81 and 85.

Even if moisture is not taken in, HF is produced from H that is inherently contained in the FSG layer 81. Furthermore, HF is also produced by reaction of hydrogen (H) and moisture ( $H_2O$ ) in silicon nitride layers 84 and 88 with surplus fluorine (F) in FSG layers 81 and 85. FSG layers 81 and 85 and silicon nitride layers 84 and 88 contain H, because gaseous materials such as silane and ammonia containing H are employed as source gas, and this H is mixed into FSG layers 81/85 and silicon nitride layers 84/88.

The above-noted HF will cause corrosion of Cu

interconnections 83/87 or barrier metal layers 82/86,  
and degrade adhesion between Cu interconnections 83/87  
and insulating layers 81/84/85/88. Further, this  
corrosion and deteriorated adhesion will cause more  
5 serious problems, for example, layer peeling off,  
bonding durability decline and decrease in reliability.

As described above, it has been proposed to use  
an FSG layer in interconnections as an insulating layer  
with low permittivity, to prevent signal transmission  
10 delay. However, there is a problem in using an FSG  
layer, that is, moisture absorption is high and HF is  
generated, causing corrosion of interconnection itself  
or barrier metal layer or peeling off of layers. Thus,  
a semiconductor device employing fluorine-doped silicon  
15 oxide as an insulating layer for interconnections and  
including multi-layer interconnection to decrease the  
influence of HF, and a method of manufacturing the same  
have been expected.

#### BRIEF SUMMARY OF THE INVENTION

20 A semiconductor device according to a first aspect  
of the present invention comprises:

a semiconductor substrate;

an interlayer insulating layer formed above the  
semiconductor substrate;

25 a first metal interconnection embedded in the  
interlayer insulating layer with a surface thereof  
exposed to substantially the same plane as a surface of

the interlayer insulating layer;

a diffusion preventive layer formed on at least the metal interconnection to prevent diffusion of a metal included in the first metal interconnection;

5 a nitrogen-doped silicon oxide layer formed on the diffusion preventive layer;

a fluorine-doped silicon oxide layer formed on the nitrogen-doped silicon oxide layer; and

10 a second metal interconnection embedded in the fluorine-doped silicon oxide layer with a surface thereof exposed to substantially the same plane as a surface of the fluorine-doped silicon oxide layer, and electrically connected to the first metal interconnection.

15 A semiconductor device according to a second aspect of the invention comprises:

a semiconductor substrate;

an interlayer insulating layer formed above the semiconductor substrate;

20 a first metal interconnection embedded in the interlayer insulating layer with a surface thereof exposed to substantially the same plane as a surface of the interlayer insulating layer;

a diffusion preventive layer formed on at least the metal interconnection to prevent diffusion of a metal included in the first metal interconnection;

25 a first nitrogen-doped silicon oxide layer formed

on the diffusion preventive layer;

a fluorine-doped silicon oxide layer formed on the first nitrogen-doped silicon oxide layer;

5 a second nitrogen-doped silicon oxide layer formed on the fluorine-doped silicon oxide layer; and

a second metal interconnection embedded in the fluorine-doped silicon oxide layer with a surface thereof exposed to substantially the same plane as a surface of the second nitrogen-doped silicon oxide layer, penetrating through the second nitrogen-doped silicon oxide layer, and electrically connected to the first metal interconnection.

A semiconductor device manufacturing method according to a third aspect of the invention comprises:  
15 embedding an under interconnection layer in an interlayer insulating layer such that a surface thereof is exposed to substantially the same plane as a surface of the interlayer insulating layer;

forming a diffusion preventive layer to prevent  
20 diffusion of a metal included in the under interconnection layer, on at least the under interconnection layer;

forming a first nitrogen-doped silicon oxide layer on the diffusion preventive layer;

25 forming a fluorine-doped silicon oxide layer on the nitrogen-doped silicon oxide layer;

forming an interconnection groove and a via hole

extending from a bottom of the interconnection groove above the under interconnection layer in the fluorine-doped silicon oxide layer; and

forming a plug in the via hole with a metal layer, to be in electrically contact with the under interconnection layer, and an upper interconnection layer in the interconnection groove with the metal layer, to be electrically contact with the plug.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

FIG. 1 is a sectional view of Cu multi-layer interconnection employing a conventional FSG layer.

FIGS. 2A - 2F are sectional views illustrating the steps of manufacturing Cu multi-layer interconnection in accordance with a first embodiment.

FIG. 3 is a perspective view showing a parallel plate CVD system used for manufacturing the Cu multi-layer interconnection in the first embodiment.

FIG. 4A is a sectional view of a conventional multi-layer substrate not including an SiON layer.

FIG. 4B is a graph showing a diffusion profile of Si, H, F and O when a specimen shown in FIG. 4A is heated in an annealing furnace in atmosphere of N<sub>2</sub> gas at atmospheric pressure.

FIG. 5A is a sectional view of a multi-layer substrate including an SiON layer of the first embodiment.

FIG. 5B is a graph showing a diffusion profile of

Si, H, F and O when a specimen shown in FIG. 5A is heated in an annealing furnace in atmosphere of N<sub>2</sub> gas at atmospheric pressure.

5        FIG. 6 is a graph showing a relationship between a refractive index of an SiON layer measured with a He-Ne laser of 633 nm and a diffusion distance of fluorine heated in an annealing furnace in atmosphere of N<sub>2</sub> gas at atmospheric pressure.

10       FIG. 7 is a graph showing a relationship between a refractive index and N composition of an SiON layer.

FIGS. 8A - 8D are sectional views illustrating the steps of manufacturing Cu multi-layer interconnection in accordance with a second embodiment.

#### DETAILED DESCRIPTION OF THE INVENTION

15       Hereinafter embodiments of the present invention will be explained with reference to the accompanying drawings.

(First embodiment)

20       FIGS. 2A - 2F are sectional views illustrating the steps of manufacturing Cu multi-layer interconnection in accordance with a first embodiment.

FIG. 2A illustrates in cross section a first Cu interconnection structure formed by a known damascene process. The first Cu interconnection structure  
25       comprises a first interlayer insulating layer 1 with an interconnection groove on its surface, a first barrier metal layer 2 covering the bottom and sides of



the interconnection groove, a first Cu interconnection  
(under interconnection layer) 3 embedded in the  
interconnection groove, and a first silicon nitride  
layer 4 formed as a Cu diffusion preventive layer on  
5 the first interlayer insulating layer 1.

The above first Cu interconnection structure is  
formed on an Si wafer 13. The interlayer insulating  
layer 1 is an FSG layer, for example. In this case,  
it is desirable to form a nitrogen-doped silicon oxide  
10 layer 14 between the interlayer insulating layer 1 and  
Si wafer 13. The nitrogen-doped silicon oxide layer 14  
precludes moisture supposed to be contained in the Si  
wafer 13 from penetrating into the FSG layer 1.

In addition, it is more desirable to form a  
15 nitrogen-doped silicon oxide layer between the  
interlayer insulating layer 1 and the first silicon  
nitride layer 4 (Cu diffusion preventive layer).  
In this case, the nitrogen-doped silicon oxide  
layer improves the adhesion strength between the  
20 interlayer insulating layer 1 and the first silicon  
nitride layer 4.

Next, as shown in FIG. 2B, a first nitrogen-doped  
silicon oxide layer (hereinafter noted SiON layer) 5 is  
formed on the first silicon nitride layer 4.

25 The SiON layer 5 is formed by means of a parallel  
plate CVD system, for example, shown in FIG. 3.  
In FIG. 3, denoted at 20 is a reaction chamber made

of metal such as aluminum (Al). Formed at the top of the reaction chamber 20 is a source gas inlet 21 to introduce source gas such as  $\text{SiH}_4$ ,  $\text{SiF}_4$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$  and  $\text{NH}_3$  into the chamber. The source gas is controlled in  
5 flow rate with a massflow controller (MFC) (not shown), and dispersed uniformly through a gas dispersion plate 22, and supplied into the reaction chamber 20.

The gas dispersion plate 22 serves also as a radio frequency (RF) electrode, and is connected to  
10 one end of a radio frequency (RF) power supply 23. The other end of the RF power supply 23 is grounded. By supplying electric power to the RF power supply 23, capacitive coupling occurs, and electric power is supplied to the space in the reaction chamber 20,  
15 and plasma is produced.

A substrate grounding electrode 24 can hold an Si wafer 25 as a susceptor, and is supported by a lift mechanism so as to control the distance between the Si wafer 25 and the gas dispersion plate 22 which acts as  
20 an upper electrode. Further, the substrate grounding electrode 24 includes a heater 26 to control the temperature of the Si wafer 25 up to about  $450^\circ\text{C}$ .

Also connected to the reaction chamber 20 is a dry pump 27 which evacuates the chamber 20 and regulates  
25 the pressure in the chamber 20 through a throttle valve 28.

Description will now be given on the method of

creating an SiON layer 5 by using the aforementioned parallel plate CVD system.

First, an Si wafer 25 is introduced into the reaction chamber 20, and held on the substrate grounding electrode 24. Next, source gas, for example, SiH<sub>4</sub> gas of 50 SCCM, N<sub>2</sub>O of 500 SCCM and N<sub>2</sub> of 3000 SCCM are led into the reaction chamber 20, and then the pressure in the chamber 20 is regulated to approximately 400 Pa (= 3 torr). And, when the pressure and gas flow rate become stable, electric power of 350 watts is supplied to the RF power supply 23. An SiON layer 5 with a thickness of 10 - 100 nm will be formed.

Next, as shown in FIG. 2B, an FSG layer 6 is formed on the SiON layer 5. A concrete method of forming the FSG layer 6 will be explained below.

First, an Si wafer 25 is placed in and held on the substrate grounding electrode 24 in the reaction chamber 20 of the parallel plate CVD system shown in FIG. 3. Next, source gas, for example, SiH<sub>4</sub> gas of 100 SCCM, N<sub>2</sub>O of 2500 SCCM and SiF<sub>4</sub> of 200 SCCM are introduced into the reaction chamber 20, and then the pressure in the chamber 20 is regulated to approximately 667 Pa (= 5 torr). And, when the pressure and gas flow rate become stable, electric power of 1500 watts is supplied to the RF power supply 23. An FSG layer with a fluorine density of 4 - 12 atomic % and

thickness of 100 - 1500 nm will be formed to match a desired interlayer thickness.

Finally, a second SiON layer 7 is formed on the FSG layer 6. A concrete method of forming the SiON layer 7 will be explained below.

First, an Si wafer 25 is placed in and held on the substrate grounding electrode 24 in the reaction chamber 20 of the parallel plate CVD system shown in FIG. 3. Next, source gas, for example, SiH<sub>4</sub> gas of 50 SCCM, N<sub>2</sub>O of 500 SCCM and N<sub>2</sub> of 3000 SCCM are introduced into the reaction chamber 20, and then the pressure in the chamber 20 is regulated to approximately 400 Pa (= 3 torr). And, when the pressure and gas flow rate become stable, electric power of 350 watts is supplied to the RF power supply 23. An SiON layer 7 with a thickness of 200 - 300 nm will be formed.

Next, as shown in FIG. 2C, an interlayer insulating layer for a silicon nitride layer 4, SiON layer 5, FSG layer 6 and SiON layer 7 is processed by known photolithography and reactive ion etching (RIE), thereby forming an interconnection groove 8 on the surfaces of the interlayer insulating layers 4 - 7, and a via hole 9 is formed to connect the bottom of interconnection groove 8 to the surface of Cu interconnection 3. The interconnection groove 8 runs through the SiON layer 7, and the bottom of the

interconnection groove 8 presents in the FSG layer 6.

No particular order is specified in forming the interconnection groove 8 and via hole 9. When the via hole 9 is formed first, a photoresist pattern having  
5 a window for the via hole 9 shall be formed on the SiON layer 7, and through this pattern as a mask, reactive ion etching (RIE) is enforced on the interlayer insulating layers 4 ~ 7, whereby a via hole 9 is formed. Next, the above photo resist pattern is  
10 stripped off, a resist pattern having a window for the interconnection groove 8 is formed on the SiON layer 7, and through this pattern as a mask, reactive ion etching (RIE) is performed on the FSG layer 6 and SiON layer 7, whereby an interconnection groove 8 is formed.

15 Next, as shown in FIGS. 2C and 2D, a second barrier metal layer 10 is deposited to cover all over the surface of the interconnection groove 8 and via hole 9, and a via plug and Cu layer 11 as an interconnection layer are formed so as to fill up the interior  
20 in the interconnection groove 8 and via hole 9.

A second barrier metal layer 10 is formed by sputtering or metal organic CVD (MOCVD), for example. The Cu layer 11 is, on the other hand, is formed by forming a Cu thin film as a plating seed by the  
25 sputtering technique, and a Cu film, as interconnection itself, is piled up to a desired thickness on the Cu thin film by using a plating technique.

Finally, as shown in FIG. 2E, the Cu layer 11 and barrier metal layer 10 formed outside the interconnection groove 8 and via hole 9 are removed by chemical mechanical polishing (CMP) to flatten the surface of the structure. The thickness of residual Cu layer 11 is 200 - 1000 nm. In this way, a second interconnection (upper interconnection layer) 11 and an inter-line via plug which electrically connects the first Cu interconnection 3 to the second Cu interconnection 11 are completed. In this arrangement, the Cu interconnection 11 is dual damascene interconnection, but it may also be so called single damascene interconnection. Likewise, the Cu interconnection 3 may be either dual damascene interconnection or single damascene interconnection. In the CMP based process of removing the Cu layer 11 and barrier metal layer 10 formed outside the interconnection groove 8 and via hole 9, considering a polishing margin and the like on the wafer surface, it is allowable to remove a part of the SiON layer 7.

Thereafter, as shown in FIG. 2F, a second silicon nitride layer 12, as a Cu diffusion preventive layer, is formed on the SiON layer 7, barrier metal layer 10 and Cu interconnection 11.

FIGS. 4B and 5B graphically show diffusion profiles of Si, H, F and O, respectively, when a specimen not including SiON layer (prior art) and a

specimen including SiON layer (the embodiment discussed here) are heated for 2 hours in an annealing furnace at 450°C in atmosphere of N<sub>2</sub> gas at atmospheric pressure. In this time, the refractive indexes of SiON layers 5 and 7 measured with a He-Ne laser of 633 nm are 1.52. FIGS. 4A and 5A show sectional views of these specimens, respectively. In these figures, the same reference numbers are given to the same components as those in FIG. 2.

With the specimen not including SiON layers 5 and 7 (FIGS. 4A and 4B), pile-up of high concentration F is seen in the interfaces between silicon nitride layers 4/12 and FSG layer 6. This is caused by that free fluorine (F) contained in the FSG layer 6 moves to the interfaces during the heating process.

Conversely, with the specimen including SiON layers 5 and 7 (FIGS. 5A and 5B), pile-up of high concentration F is not seen in the interfaces between silicon nitride layers 4/12 and SiON layers 5/7 and the interfaces between SiON layers 5/7 and FSG layer 6. This is caused by free fluorine (F) contained in the FSG layer 6 diffusing to SiON layers 5 and 7, which are upper and lower layers, and remains thereon.

Therefore, according to the first embodiment, free fluorine (F) contained in the FSG layer 6 can be sufficiently absorbed into SiON layers 5 and 7, and the amount of HF produced as a result of chemical reaction

of fluorine (F) and hydrogen (H) can be substantially decreased. This contributes to prevent corrosion of Cu interconnections 3/11 and barrier metal layers 2/10 formed on the FSG layer 6. This also prevents  
5 deterioration of adhesion of the Cu interconnections 11 and barrier metal layer 10 to the insulating layers 4, 5, 6, 7 and 12, as well as preventing peeling off of layers during the CMP process in FIG. 2E and the processes involving the heating step. The processes  
10 involving a heating step include, for example, annealing to increase grain size in the Cu interconnections 3/11, heating involved in the step of forming an insulating layer which is formed after the Cu interconnection 11, annealing to regulate the threshold  
15 voltage of MOS transistors, and so on.

FIG. 6 graphically shows a refractive index of SiON layers 5 and 7 measured with an He-Ne laser of 633 nm and a diffusion fluorine layer thickness when heated for 0 - 20 minutes in an annealing furnace  
20 at 450°C in an atmosphere of N<sub>2</sub> gas at atmospheric pressure.

It will be apparent from FIG. 6 that when the refractive index of SiON layers 5/7 is 1.4, namely, the refractive index is low, the F diffusion distance  
25 increases. This may be caused by surplus free fluorine (F) not being sufficiently absorbed. As the F diffusion distance increases, the adhesion decreases.



On the other hand, it is seen that when the refractive index is 1.50 or higher, the F diffusion distance becomes sufficiently small. Therefore, it is desirable to set the refractive index of SiON layer 5/7 to 1.50 or higher.

In addition, when the refractive index of SiON layers 5/7 is high, the permittivity of SiON layers 5/7 increases. This induces the increased capacitance between interconnections and between interconnection layers, and delays the operating speed of a semiconductor device. Therefore, it is desirable to set the refractive index of SiON layers 5/7 to 1.55 or lower.

FIG. 7 graphically shows a relationship between the refractive index and N composition of an SiON layer, which is determined by X-ray photoelectron spectroscopy (XPS). It is seen from FIG. 7 that the refractive index 1.50 corresponds to the N composition 6 and the index 1.55 corresponds to the N composition 10.5 (atomic %), respectively. Therefore, to produce an SiON layer with a refractive index 1.50 - 1.55, it is necessary to create an SiON layer with a nitride density of 6 - 10.5 atomic % by controlling nitride or other materials used.

Thereafter, the steps of forming the interlayer insulating layers 5 - 12, barrier metal layer 10 and Cu interconnection 11 are repeated to create a multilayer Cu interconnection comprising 4 to 8 layers, whereby

the adhesion between of the Cu interconnection 11 and barrier metal layer 10 to the interlayer insulating layers 5 - 12 is improved, and a semiconductor device with ensured heat stability and mechanical strength is realized.

(Second embodiment)

FIGS. 8A - 8D are sectional views illustrating a method of manufacturing a multi-layer Cu interconnection according to a second embodiment. In these figures, like reference numerals indicate corresponding parts in FIGS. 2A - 2F, and detail explanation is omitted. Only the difference of the second embodiment from the first embodiment is that a second SiON layer 7 is present during manufacturing, but is eliminated in the final structure.

First, as shown in FIG. 8A, SiON layer 5, FSG layer 6 and SiON layer 7 are formed on a first silicon nitride layer 4, as in the first embodiment. Method, system and conditions for forming these layers 5 - 7 are the same as those in the first embodiment, except the thickness of SiON layer 7 is 50 - 100 nm while 200 - 300 nm in the first embodiment.

Next, as shown in FIG. 8B, the interconnection groove 8, via hole 9, barrier metal layer 10 and Cu layer 11 are formed, as in the first embodiment. As the SiON layer 7 is 50 - 100 nm thick, it is easy, as compared with the first embodiment, to process the

insulating layer which forms the interconnection groove 8 and via hole 9, and the embedding of Cu layer 1 into the interconnection groove 8 and via hole 9 is also easy.

5           Next, as shown in FIG. 8C, the Cu layer 11, barrier metal layer 10 and SiON layer 7 formed outside the interconnection groove 8 and via hole 9 are removed by the CMP technique to flatten the surface of the structure. As the SiON layer 7 is as thin as  
10       50 - 100 nm, the removal of this layer is easy.

          Next, as shown FIG. 8D, silicon nitride layer 12 is formed on FSG layer 7, barrier metal layer 10 and Cu interconnection 11. After this, as in the first embodiment, the steps of forming the interlayer  
15       insulating layers 5 - 12, barrier metal layer 10 and Cu interconnection 11 are repeated to create a multi-layer Cu interconnection comprising 4 to 8 layers.

          In accordance with the present embodiment, unwanted capacitance increase between interconnections  
20       or between interconnection layers can be effectively suppressed. Additionally, the same effects as in the first embodiment can be obtained. The SiON layer 7 may be omitted unless peeling-off due to moisture absorption after being left is expected.

25           The invention is not to be limited by the embodiments described herein. For example, in the embodiments, Cu interconnection is discussed, but

it may alternatively be Al or another metal interconnection.

Note that Al interconnection processed by RIE is surrounded by SiON with high permittivity, and if spacing in adjacent interconnections is limited, the interline effective permittivity ( $K_{eff}$ ) becomes relatively high. Therefore, when spacing is limited in the interconnections, it is advantageous from the viewpoint of interline permittivity to employ Cu damascene interconnection whose upper surface is covered by an SiON layer or SiN layer.

Further, as a diffusion preventive layer, a silicon carbide layer may be used instead of a silicon nitride layer. Also, the Si wafer may be replaced by other semiconductor wafers such as SOI and SiGe wafers.

As described in detail above, the present invention realizes a semiconductor device which includes a multi-layer interconnection employing a fluorine-doped silicon oxide layer as an insulating layer between interconnections to reduce the influence of HF, and a method of manufacturing the same.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the

spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.